Wave function and external potential from constrained search in density-functional theory

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It is proven that in Levy's constrained search or Lieb's ensemble constrained search, if the minimum is achieved by wave functions that satisfy the steadiness condition for the current density kernel and have continuous second derivatives, the minimizing wave functions are eigenstates of some external potential. If the excited states of this potential can only achieve stationarity and cannot achieve a minimum in the constrained search, the minimizing wave functions are ground states and the corresponding electron density is v-representable or ensemble v-representable. This is also true for the ensemble system with a varying electron number. In time-dependent density-functional theory, if the stationarity of the action integral is achieved in the constrained search by a wave function that satisfies the continuity equation for the current density kernel and has a continuous first derivative with respect to the time coordinate and continuous second derivatives with respect to the space coordinates, the stationary wave function satisfies the time-dependent Schrödinger equation of some time-dependent external potential and the corresponding electron density is time-dependent v-representable.

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I. INTRODUCTION

The wave function, electron density, and external potential are three essential quantities involved in density-functional theory (DFT) [1,2]. Their interrelation is the core of DFT. Because the ground-state electron density uniquely determines the external potential, emphasis was placed on the electron density instead of the wave function [1]. Because the ground-state electron density minimizes the energy functional, a Kohn-Sham (KS) scheme was established to obtain this density [2]. The DFT energy functional is defined in terms of constrained search [3–6]. By its definition, constrained search does not explicitly include any external potential, and the minimizing wave function is completely determined by the corresponding electron density. Further investigation of the interrelation between the electron density, the minimizing wave function, and a possible external potential is still an interesting and open problem. For instance, is it true that the minimizing wave function is a ground state of some external potential? What are the conditions for this proposition? How could we prove it? What could we conclude for the stationary wave function as well? What is the conclusion in the time-dependent (TD) case?

Answers to these questions are of significance in quantum mechanics, because they relate the wave function to a possible external potential and thus provide useful clues for finding the target electron density and the corresponding wave function. In DFT, they may also provide at least indirect conditions for v-representability. The v-representability problem is closely related to the differentiability of DFT functionals [6], and there still lacks complete understanding [6–8]. Thus solution of a recent debate about whether the kinetic functional derivative is a local function, for instance, relies on v-representability [9–17]. The relationship between the highest occupied KS orbital energy and the ionization energy in ensemble extension is also related to v-representability, since it helps to eliminate the doubt about the differentiability of the ensemble functional and the existence of a KS potential [18–22]. In time-dependent DFT (TDDFT), the v-representability problem is even more important because most TDDFT action functionals are defined only for TD v-representable densities [23,24]. Conditions for v-representability are unknown [6,25] and the progress is scarce [26].

In this work, the following conclusions are directly proven: If the minimum in the constrained search of Levy [3,4] is achieved by a wave function that satisfies the steadiness condition for the current density kernel and has continuous second derivatives with respect to the space coordinates, the minimizing wave function is an eigenstate of some external potential. Similarly, if the minimum in the ensemble constrained search of Lieb [5,6] is achieved by a set of wave functions each of which satisfies the steadiness condition for the current density kernel and has continuous second derivatives with respect to the space coordinates, every wave function in this set is an eigenstate of some external potential. If the excited states of the related external potential can only achieve stationarity and cannot achieve a minimum in the constrained search, the minimizing wave functions are ground states and the corresponding electron density is v-representable in Levy's case or ensemble v-representable in Lieb's case. The conclusion also applies to the ensemble system with a varying electron number introduced by Perdew *et al.* [18,20]. Generally, if the stationarity in the constrained search is achieved by wave functions that satisfy the steadiness condition for the current density kernel and have continuous second derivatives with respect to the space coordinates, the stationary wave functions are eigenstates of some external potential. In TDDFT, if the stationarity of the action integral [23,27] is achieved in the constrained search by a TD wave function that satisfies the continuity equation for the current density kernel and has a continuous first derivative with respect to the time coordinate and continuous second derivatives with respect to the space coordinates, the

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stationary wave function satisfies the TD Schrödinger equation of some TD external potential and the corresponding electron density is TD v-representable. The proof of these conclusions demonstrates the importance of the fact that the first-order variation of the functional integrals in the constrained search vanishes at the minimizing or stationary wave functions.

II. DERIVATION

A. Basic case

Suppose in atomic units, $\hat{T}=\Sigma_{i=1}^{N}(-1/2)\nabla_i^2$ and $\hat{U}=\Sigma_{1\le i<j\le N}1/|\vec{r}_j-\vec{r}_i|$ are the kinetic and electron-electron repelling operators of the N-electron system, respectively. The DFT universal functional is defined by Levy's constrained search [3,4],

$$F[\rho]=\min_{\psi\Rightarrow\rho}\langle\psi|\hat{T}+\hat{U}|\psi\rangle, \tag{1}$$

where the normalized antisymmetric trial wave functions generate the electron density $\rho(\vec{r})$. It has been proven that the minimum can always be achieved by a wave function [5,6]. However, for bound states the kinetic energy is calculated by $\langle\psi|\hat{T}|\psi\rangle=(1/2)\Sigma_{i=1}^{N}\int\nabla_i\psi^*\cdot\nabla_i\psi d\vec{r}_1\cdots d\vec{r}_N$. Hence trial functions in Eq. (1) belong to a Sobolev space $H_1(R^{3N})$, meaning that they are only required to have integrable first derivatives [6]. More importantly, a true static wave function must satisfy the steadiness condition,

$$\sum_{k=1}^{N}\nabla_k\cdot\vec{j}_k(\vec{r}_1,\ldots,\vec{r}_N)=0, \tag{2}$$

where $\vec{j}_k(\vec{r}_1,\ldots,\vec{r}_N)=(-i/2)(\psi^*\nabla_k\psi-\psi\nabla_k\psi^*)$ is the current density kernel and $k=1,\ldots,N$. Because the static Schrödinger equation requires second derivatives of wave functions and Eq. (2) should be satisfied, generally the minimizing wave function may not be an eigenstate of some external potential. Now suppose that for a density $\rho(\vec{r})$, the minimum of $\langle\psi|\hat{T}+\hat{U}|\psi\rangle$ is achieved by a wave function ψ that satisfies Eq. (2) and has continuous second derivatives. One can define a function ϕ as

$$\phi(\vec{r}_1,\ldots,\vec{r}_N)=\frac{(\hat{T}+\hat{U})\psi(\vec{r}_1,\ldots,\vec{r}_N)}{\psi(\vec{r}_1,\ldots,\vec{r}_N)} \tag{3}$$

for $\psi(\vec{r}_1,\ldots,\vec{r}_N)\neq 0$. If necessary, ϕ can be defined by a limit process for $\psi=0$. Because Eq. (2) means $\psi^*\hat{T}\psi-\psi\hat{T}\psi^*=0$ and thus $\hat{T}\psi^*/\psi^*=\hat{T}\psi/\psi$, ϕ is a real function. ϕ is also symmetric and continuous if $\psi\neq 0$. We prove that the vanishing first-order variation of $\langle\psi|\hat{T}+\hat{U}|\psi\rangle$, the normalization of wave functions, and the condition that trial wave functions generate the same density jointly dictate that ϕ must have the form

$$\phi(\vec{r}_1,\ldots,\vec{r}_N)=\sum_{i=1}^{N}u(\vec{r}_i), \tag{4}$$

where $u(\vec{r})$ is a real function of the spatial position.

At the minimizing wave function $\psi(\vec{r}_1,\ldots,\vec{r}_N)$, the first-order variation of $\langle\psi|\hat{T}+\hat{U}|\psi\rangle$ must be zero; that is, $\langle\psi+\delta\psi|\hat{T}+\hat{U}|\psi+\delta\psi\rangle-\langle\psi|\hat{T}+\hat{U}|\psi\rangle$ must be a higher-order infinitesimal of $\int|\delta\psi|d\vec{r}_1\cdots d\vec{r}_N$ for $\psi+\delta\psi$ that generates $\rho(\vec{r})$. According to the definition of ϕ, this means that for $\delta(\psi^*\psi)=(\psi^*+\delta\psi^*)(\psi+\delta\psi)-\psi^*\psi$, the integral $\int\phi\delta(\psi^*\psi)d\vec{r}_1\cdots d\vec{r}_N$ is also a higher-order infinitesimal, or $\lim_{\delta\psi\to 0}[\int\phi\delta(\psi^*\psi)d\vec{r}_1\cdots d\vec{r}_N/\int|\delta\psi|d\vec{r}_1\cdots d\vec{r}_N]=0$. Normalization of ψ and $\psi+\delta\psi$ requires

$$\int\delta(\psi^*\psi)d\vec{r}_1\cdots d\vec{r}_N=0. \tag{5}$$

Furthermore, both ψ and $\psi+\delta\psi$ generate the same density $\rho(\vec{r})$. Hence

$$\delta\rho(\vec{r})=N\int\delta(\psi^*\psi)d\vec{r}_2\cdots d\vec{r}_N=0 \tag{6}$$

for any $\vec{r}$. To prove Eq. (4), we choose $2N$ different fixed points $\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N$ and $\vec{r}'_1,\vec{r}'_2,\ldots,\vec{r}'_N$. We then take $2N$ small nonoverlapping regions $V_1,V_2,\ldots,V_N$ and $V'_1,V'_2,\ldots,V'_N$ that, respectively, surround these points. We suppose that all four values $\psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$, $\psi(\vec{r}_1,\vec{r}'_2,\ldots,\vec{r}'_N)$, $\psi(\vec{r}'_1,\vec{r}_2,\ldots,\vec{r}_N)$, and $\psi(\vec{r}'_1,\vec{r}'_2,\ldots,\vec{r}'_N)$ are nonzero. Hence ϕ is continuous at $(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$, $(\vec{r}_1,\vec{r}'_2,\ldots,\vec{r}'_N)$, $(\vec{r}'_1,\vec{r}_2,\ldots,\vec{r}_N)$, and $(\vec{r}'_1,\vec{r}'_2,\ldots,\vec{r}'_N)$. One can always choose $\delta\psi$ such that $\delta(\psi^*\psi)$ is nonzero only in the following four sets of $3N$-dimensional regions: $V_1\times V_2\times\cdots\times V_N$ and its permutations, $V_1\times V'_2\times\cdots\times V'_N$ and its permutations, $V'_1\times V_2\times\cdots\times V_N$ and its permutations, and finally $V'_1\times V'_2\times\cdots\times V'_N$ and its permutations. Permutations are considered because $\delta(\psi^*\psi)$ is symmetric. Specifically, we choose $\delta\psi$ such that $\delta(\psi^*\psi)>0$ in the first and fourth sets of regions and $\delta(\psi^*\psi)<0$ in the second and third sets of regions. We require that $\delta\psi\to 0$ as V_i shrinks to $\vec{r}_i$ and V'_1 shrinks to $\vec{r}'_i$, that is, $V_i\to\vec{r}_i$ and $V'_i\to\vec{r}'_i$, $i=1,2,\ldots,N$. For Eq. (6) to be satisfied, we further require

$$\delta\rho(\vec{r})=N!\int_{V_2\times\cdots\times V_N}\delta(\psi^*\psi)d\vec{r}_2\cdots d\vec{r}_N+N!\int_{V'_2\times\cdots\times V'_N}\delta(\psi^*\psi)d\vec{r}_2\cdots d\vec{r}_N=0 \tag{7}$$

for $\vec{r}\in V_1$ or $\vec{r}\in V'_1$,

$$\delta\rho(\vec{r})=N!\int_{V_1\times\cdots\times V_{i-1}\times V_{i+1}\times\cdots\times V_N}\delta(\psi^*\psi)d\vec{r}_2\cdots d\vec{r}_N+N!\int_{V'_1\times V_2\times\cdots\times V_{i-1}\times V_{i+1}\times\cdots\times V_N}\delta(\psi^*\psi)d\vec{r}_2\cdots d\vec{r}_N=0 \tag{8}$$

for $\vec{r}\in V_i$, $i=2,3,\ldots,N$, and

$$\delta\rho(\vec{r}) = N! \int_{V_1\times V_2'\times\cdots\times V_{i-1}'\times V_{i+1}'\times\cdots\times V_N'} \delta(\psi^*\psi)d\vec{r}_2\cdots d\vec{r}_N + N! \int_{V_1'\times\cdots\times V_{i-1}'\times V_{i+1}'\times\cdots\times V_N'} \delta(\psi^*\psi)d\vec{r}_2\cdots d\vec{r}_N = 0 \tag{9}$$

for $\vec{r}\in V_i'$, $i=2,3,\ldots,N$. To satisfy Eqs. (7)–(9), we may simply let all the small regions be a spheroid centered at different fixed points, and let $\delta(\psi^*\psi)$ be a product of the same spatial function centered at different fixed points in every above-mentioned $3N$-dimensional region. Zero values of these equations are guaranteed by appending different signs to the products for different $3N$-dimensional regions. We define

$$I_1 = \int_{V_1\times V_2\times\cdots\times V_N} \delta(\psi^*\psi)d\vec{r}_1\cdots d\vec{r}_N,$$

$$I_2 = \int_{V_1\times V_2'\times\cdots\times V_N'} \delta(\psi^*\psi)d\vec{r}_1\cdots d\vec{r}_N,$$

$$I_3 = \int_{V_1'\times V_2\times\cdots\times V_N} \delta(\psi^*\psi)d\vec{r}_1\cdots d\vec{r}_N,$$

and

$$I_4 = \int_{V_1'\times V_2'\times\cdots\times V_N'} \delta(\psi^*\psi)d\vec{r}_1\cdots d\vec{r}_N.$$

Equations (7)–(9) lead to

$$I_1 = -I_2 = -I_3 = I_4 = \frac{1}{4\times N!}\int |\delta(\psi^*\psi)|d\vec{r}_1\cdots d\vec{r}_N. \tag{10}$$

Equation (10) guarantees Eq. (5) since $\int\delta(\psi^*\psi)d\vec{r}_1\cdots d\vec{r}_N = N!(I_1+I_2+I_3+I_4)=0$. Because ϕ is continuous and $\delta(\psi^*\psi)$ maintains its sign in every $3N$-dimensional region, one can apply the intermediate-value theorem of integrals [28] and obtain, for instance,

$$\int_{V_1\times V_2\times\cdots\times V_N} \phi\delta(\psi^*\psi)d\vec{r}_1\cdots d\vec{r}_N = \phi(\vec{r}_1'',\vec{r}_2'',\ldots,\vec{r}_N'')\int_{V_1\times V_2\times\cdots\times V_N}\delta(\psi^*\psi)d\vec{r}_1\cdots d\vec{r}_N = \phi(\vec{r}_1'',\vec{r}_2'',\ldots,\vec{r}_N'')I_1,$$

where $\vec{r}_i''$ is a point in V_i, $i=1,2,\ldots,N$. In general, $\vec{r}_i''\neq\vec{r}_i$. However, it is obvious that $\vec{r}_i''\to\vec{r}_i$ as $V_i\to\vec{r}_i$, $i=1,2,\ldots,N$. Now we define $\varepsilon_1=\phi(\vec{r}_1'',\vec{r}_2'',\ldots,\vec{r}_N'')-\phi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$ and use the expression $\phi(\vec{r}_1'',\vec{r}_2'',\ldots,\vec{r}_N'')I_1=[\phi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)+\varepsilon_1]I_1$. Because ϕ is continuous, one concludes $\phi(\vec{r}_1'',\vec{r}_2'',\ldots,\vec{r}_N'')\to\phi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$ and thus $\varepsilon_1\to 0$ as $V_i\to\vec{r}_i$, $i=1,2,\ldots,N$. Hence according to the intermediate-value theorem of integrals and Eq. (10), one obtains

$$\begin{aligned}
&\int \phi\delta(\psi^*\psi)d\vec{r}_1\cdots d\vec{r}_N \\
&= N!\left[\int_{V_1\times V_2\times\cdots\times V_N}\phi\delta(\psi^*\psi)d\vec{r}_1\cdots d\vec{r}_N + \int_{V_1\times V_2'\times\cdots\times V_N'}\phi\delta(\psi^*\psi)d\vec{r}_1\cdots d\vec{r}_N + \int_{V_1'\times V_2\times\cdots\times V_N}\phi\delta(\psi^*\psi)d\vec{r}_1\cdots d\vec{r}_N + \int_{V_1'\times V_2'\times\cdots\times V_N'}\phi\delta(\psi^*\psi)d\vec{r}_1\cdots d\vec{r}_N\right] \\
&= N!\{[\phi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)+\varepsilon_1]I_1 + [\phi(\vec{r}_1,\vec{r}_2',\ldots,\vec{r}_N')+\varepsilon_2]I_2 + [\phi(\vec{r}_1',\vec{r}_2,\ldots,\vec{r}_N)+\varepsilon_3]I_3 + [\phi(\vec{r}_1',\vec{r}_2',\ldots,\vec{r}_N')+\varepsilon_4]I_4\} \\
&= \frac{1}{4}\{[\phi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)-\phi(\vec{r}_1,\vec{r}_2',\ldots,\vec{r}_N')] - [\phi(\vec{r}_1',\vec{r}_2,\ldots,\vec{r}_N)-\phi(\vec{r}_1',\vec{r}_2',\ldots,\vec{r}_N')]+\varepsilon_5\} \\
&\times\int|\delta(\psi^*\psi)|d\vec{r}_1\cdots d\vec{r}_N,
\end{aligned} \tag{11}$$

where $\varepsilon_5=\varepsilon_1-\varepsilon_2-\varepsilon_3+\varepsilon_4$ and $\varepsilon_i\to 0$, $i=1,2,3,4,5$, as $V_i\to\vec{r}_i$ and $V_i'\to\vec{r}_i'$, $i=1,2,\ldots,N$. We note that $\int|\delta(\psi^*\psi)|d\vec{r}_1\cdots d\vec{r}_N$ has a part that is first order in $\int|\delta\psi|d\vec{r}_1\cdots d\vec{r}_N$. However, $\int\phi\delta(\psi^*\psi)d\vec{r}_1\cdots d\vec{r}_N$ must not have a first-order part since it is a higher-order infinitesimal of $\int|\delta\psi|d\vec{r}_1\cdots d\vec{r}_N$ following the fact that ψ is the minimizing wave function. Hence from Eq. (11) one concludes that the constant $D=[\phi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)-\phi(\vec{r}_1,\vec{r}_2',\ldots,\vec{r}_N')]-[\phi(\vec{r}_1',\vec{r}_2,\ldots,\vec{r}_N)-\phi(\vec{r}_1',\vec{r}_2',\ldots,\vec{r}_N')]$ must be zero, or equivalently,

$$\phi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)-\phi(\vec{r}_1,\vec{r}_1',\ldots,\vec{r}_N') = \phi(\vec{r}_1',\vec{r}_2,\ldots,\vec{r}_N)-\phi(\vec{r}_1',\vec{r}_2',\ldots,\vec{r}_N'). \tag{12}$$

This means that $\phi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)-\phi(\vec{r}_1,\vec{r}_2',\ldots,\vec{r}_N')$ is independent of $\vec{r}_1$. Now we regard $\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N$ as arbitrary points and let $\vec{r}_1',\vec{r}_2',\ldots,\vec{r}_N'$ remain fixed. For the moment we retain the assumption that all four values $\psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$, $\psi(\vec{r}_1,\vec{r}_2',\ldots,\vec{r}_N')$, $\psi(\vec{r}_1',\vec{r}_2,\ldots,\vec{r}_N)$, and $\psi(\vec{r}_1',\vec{r}_2',\ldots,\vec{r}_N')$ are nonzero. Equation (12) then indicates that the function ϕ is $\phi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)=\phi(\vec{r}_1,\vec{r}_2',\ldots,\vec{r}_N')+\phi(\vec{r}_1',\vec{r}_2,\ldots,\vec{r}_N)-\phi(\vec{r}_1',\vec{r}_2',\ldots,\vec{r}_N')$. Since $\vec{r}_1',\vec{r}_2',\ldots,\vec{r}_N'$ are fixed, $\phi(\vec{r}_1,\vec{r}_2',\ldots,\vec{r}_N')$ is a function of $\vec{r}_1$ only; $\phi(\vec{r}_1',\vec{r}_2,\ldots,\vec{r}_N)$ is a function of $\vec{r}_2,\ldots,\vec{r}_N$ only; and $\phi(\vec{r}_1',\vec{r}_2',\ldots,\vec{r}_N')$ is a constant. This means that ϕ has the form $\phi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_3)=u(\vec{r}_1)+f_1(\vec{r}_2,\ldots,\vec{r}_N)$, where u is a function of the spatial position and f_1 is a function of $N-1$ spatial positions. Because ϕ is symmetric, by exchanging $\vec{r}_1$ and $\vec{r}_2$ one obtains $u(\vec{r}_1)+f_1(\vec{r}_2,\vec{r}_3,\ldots,\vec{r}_N)=u(\vec{r}_2)+f_1(\vec{r}_1,\vec{r}_3,\ldots,\vec{r}_N)$, or $f_1(\vec{r}_2,\vec{r}_3,\ldots,\vec{r}_N)-u(\vec{r}_2)=f_1(\vec{r}_1,\vec{r}_3,\ldots,\vec{r}_N)-u(\vec{r}_1)$. The last

equation indicates that the function $f_2(\vec{r}_3,\ldots,\vec{r}_N) \equiv f_1(\vec{r}_1,\vec{r}_3,\ldots,\vec{r}_N)-u(\vec{r}_1)$ is independent of both $\vec{r}_1$ and $\vec{r}_2$, and thus f_1 has the form

$$f_1(\vec{r}_2,\vec{r}_3,\ldots,\vec{r}_N) = u(\vec{r}_2) + [f_1(\vec{r}_1,\vec{r}_3,\ldots,\vec{r}_N) - u(\vec{r}_1)]$$
$$= u(\vec{r}_2) + f_2(\vec{r}_3,\ldots,\vec{r}_N).$$

By repeating the process, one eventually obtains Eq. (4). The function $u(\vec{r})$ is unique and the proof is as follows: If another set of functions u' and f_1' also satisfies $\phi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_3) = u'(\vec{r}_1)+f_1'(\vec{r}_2,\ldots,\vec{r}_N)$, we have $u(\vec{r}_1)-u'(\vec{r}_1)=f_1'(\vec{r}_2,\ldots,\vec{r}_N) - f_1(\vec{r}_2,\ldots,\vec{r}_N)$. This means that $u(\vec{r}_1)-u'(\vec{r}_1)$ is independent of $\vec{r}_1$. Hence u and u' can differ only by a constant C, that is, $u'(\vec{r})=u(\vec{r})+C$. Substituting this equation into Eq. (4), one has $\Sigma_{i=1}^N C=0$ and thus $C=0$. With the uniqueness of $u(\vec{r})$, we can complete the derivation by considering the case in which ψ may be zero. If one of the values $\psi(\vec{r}_1,\vec{r}_2',\ldots,\vec{r}_N')$, $\psi(\vec{r}_1',\vec{r}_2,\ldots,\vec{r}_N)$, and $\psi(\vec{r}_1',\vec{r}_2',\ldots,\vec{r}_N')$ is zero, we may choose another set of fixed points $\vec{r}_1',\vec{r}_2',\ldots,\vec{r}_N'$ such that all three values are nonzero, and one gets the same $u(\vec{r})$ from Eq. (12). If $\psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$ is zero, $\phi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$ may be obtained from the values of ϕ in the neighborhood of $(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$ by a limit process. The possible nonexistence of the limit value means that function $u(\vec{r})$ itself has discontinuity at one of $\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N$.

Equation (4) is thus proven. Expressing $u(\vec{r})$ as $E/N - v(\vec{r})$, where $\lim_{r\to\infty} v(\vec{r})=0$ for instance, one obtains from Eqs. (3) and (4) that

$$(\hat{T}+\hat{U})\psi + \psi\sum_{i=1}^{N} v(\vec{r}_i) = E\psi. \tag{13}$$

Equation (13) indicates that ψ is an eigenstate of the external potential $v(\vec{r})$. Generally, an eigenstate ψ of $v(\vec{r})$ satisfies $\langle\psi+\delta\psi|\hat{T}+\hat{U}|\psi+\delta\psi\rangle - \langle\psi|\hat{T}+\hat{U}|\psi\rangle = \langle\delta\psi|\hat{T}+\hat{U}+\Sigma_{i=1}^N v(\vec{r}_i) - E|\delta\psi\rangle$ for $\psi+\delta\psi$ that generates $\rho(\vec{r})$. Hence the first-order variation of $\langle\psi|\hat{T}+\hat{U}|\psi\rangle$ vanishes and ψ achieves stationarity in the constrained search. Furthermore, a ground state ψ minimizes $\langle\psi|\hat{T}+\hat{U}|\psi\rangle$ among wave functions generating $\rho(\vec{r})$. However, apart from the ground state, whether a general eigenstate can be a minimizing wave function in the constrained search remains an interesting problem. For exactness, we further introduce a restriction that for the obtained external potential $v(\vec{r})$, its excited states can only achieve stationarity and cannot achieve a minimum in the constrained search of $\langle\psi|\hat{T}+\hat{U}|\psi\rangle$. Conditions for this proposition are unknown. We can only conclude that with this restriction, ψ is a ground state of $v(\vec{r})$ and $\rho(\vec{r})$ is v-representable.

Derivations of Eq. (13) for the minimizing wave function in Eq. (1) have already been given with certain restrictions by Levy and Perdew [29] using the Lagrange-multiplier method to fix the density, and also by Gál [30] for $\rho(\vec{r})$ at which $F[\rho]$ is differentiable. As has been demonstrated for the noninteracting KS case by Levy and Perdew [29], and later for the general case (for instance, see [31]), Eq. (13) can be obtained by introducing a Lagrange multiplier E and a multiplier function $v(\vec{r})$ and then solving the unconditional extreme-value problem of the expression $\int\psi^*(\hat{T}+\hat{U})\psi d\vec{r}_1\cdots d\vec{r}_N + \Sigma_{i=1}^N \int v(\vec{r}_i)\psi^*\psi d\vec{r}_1\cdots d\vec{r}_N - E\int\psi^*\psi d\vec{r}_1\cdots d\vec{r}_N$ with respect to arbitrary ψ, because trial functions in Eq. (1) satisfy the normalization condition and generate the fixed density $\rho(\vec{r})$. However, the Lagrange-multiplier method is only a formal approach. In this work, we present the direct derivation of Eq. (13) starting from Eq. (1) and avoid the question about the existence and determination of the Lagrange multiplier and multiplier function. This is also constructive proof that there exists an external potential $v(\vec{r})$ of which the well-behaved minimizing wave function in Eq. (1) is an eigenstate if Eq. (2) holds.

B. Ensemble case

Lieb's ensemble universal functional is defined by [5,6]

$$F[\rho] = \min_{\{\lambda_i,\psi_i\}\Rightarrow\rho} \sum_{i=1}^{\infty} \lambda_i\langle\psi_i|\hat{T}+\hat{U}|\psi_i\rangle, \tag{14}$$

where $\{\psi_i\}$ are a set of orthonormal wave functions and $\{\lambda_i\}$ are a set of non-negative real numbers satisfying $\Sigma_{i=1}^{\infty}\lambda_i=1$. Besides, $\{\psi_i\}$ and $\{\lambda_i\}$ must satisfy

$$\sum_{i=1}^{\infty} \lambda_i N \int \psi_i^*\psi_i d\vec{r}_2\cdots d\vec{r}_N = \rho(\vec{r}). \tag{15}$$

As in the case of Levy's constrained search, the minimum in Eq. (14) is always achieved [5,6]. However, the minimizing wave functions may not be the ground-state wave functions of some external potential, since they may not satisfy Eq. (2) and may have only integrable first derivatives. Suppose a set of $\{\psi_i\}$ and $\{\lambda_i\}$ minimizes $\Sigma_{i=1}^{\infty}\lambda_i\langle\psi_i|\hat{T}+\hat{U}|\psi_i\rangle$, and every ψ_i satisfies Eq. (2) and has continuous second derivatives. In this case, one can define a function ϕ_i according to Eq. (3) for every ψ_i. We first suppose that without violating Eq. (15) and orthonormality, only one single function ψ_i takes a variation $\delta\psi_i$. One concludes that ψ_i minimizes $\langle\psi_i|\hat{T}+\hat{U}|\psi_i\rangle$ among wave functions generating density $\rho_i(\vec{r}) = N\int\psi_i^*\psi_i d\vec{r}_2\cdots d\vec{r}_N$. Hence according to the conclusion for Levy's functional, ψ_i is an eigenstate of some external potential $v_i(\vec{r})$ and the eigenenergy is E_i. To demonstrate that all $v_i(\vec{r})$ are the same for different i, we then suppose that only two functions ψ_j and ψ_k have a variation and prove $v_j(\vec{r}) = v_k(\vec{r})$. For an N-electron system, we need two fixed points $\vec{r},\vec{r}'$ and the corresponding small surrounding regions V,V'. We choose $\delta\psi_j$ and $\delta\psi_k$ such that $\delta(\psi_j^*\psi_j)>0$ in $V\times V\times\cdots\times V$, $\delta(\psi_j^*\psi_j)<0$ in $V'\times V'\times\cdots\times V'$, $\delta(\psi_k^*\psi_k)<0$ in $V\times V\times\cdots\times V$, and $\delta(\psi_k^*\psi_k)>0$ in $V'\times V'\times\cdots\times V'$. At other positions $\delta(\psi_j^*\psi_j)=\delta(\psi_k^*\psi_k)=0$. To satisfy Eq. (15), we require

$$\delta\rho(\vec{r}) = N\int_{V\times\cdots\times V} [\lambda_j\delta(\psi_j^*\psi_j) + \lambda_k\delta(\psi_k^*\psi_k)]d\vec{r}_2\cdots d\vec{r}_N = 0 \tag{16}$$

for $\vec{r}\in V$, and

$$\delta\rho(\vec{r}) = N\int_{V'\times\cdots\times V'} [\lambda_j \delta(\psi_j^*\psi_j) + \lambda_k \delta(\psi_k^*\psi_k)]d\vec{r}_2\cdots d\vec{r}_N = 0 \tag{17}$$

for $\vec{r}\in V'$. We now define $I_1^j = \int_{V\times\cdots\times V}\lambda_j\delta(\psi_j^*\psi_j)\times d\vec{r}_1\cdots d\vec{r}_N$, $I_2^j = \int_{V'\times\cdots\times V'}\lambda_j\delta(\psi_j^*\psi_j)d\vec{r}_1\cdots d\vec{r}_N$, $I_1^k = \int_{V\times\cdots\times V}\lambda_k\delta(\psi_k^*\psi_k)d\vec{r}_1\cdots d\vec{r}_N$, and $I_2^k = \int_{V'\times\cdots\times V'}\lambda_k\delta(\psi_k^*\psi_k)d\vec{r}_1\cdots d\vec{r}_N$. Equations (16) and (17), along with the normalization condition lead to

$$I_1^j = -I_1^k = -I_2^j = I_2^k = \frac{1}{2N}\int [\lambda_j|\delta(\psi_j^*\psi_j)| + \lambda_k|\delta(\psi_k^*\psi_k)|]d\vec{r}_1\cdots d\vec{r}_N. \tag{18}$$

Since ϕ_j and ϕ_k already have the form of Eq. (4), by applying the intermediate-value theorem of integrals and from Eq. (18), one obtains

$$\begin{aligned}
&\lambda_j\int \phi_j\delta(\psi_j^*\psi_j)d\vec{r}_1\cdots d\vec{r}_N + \lambda_k\int \phi_k\delta(\psi_k^*\psi_k)d\vec{r}_1\cdots d\vec{r}_N \\
&= [Nu_j(\vec{r}) + \varepsilon_1]I_1^j + [Nu_j(\vec{r}') + \varepsilon_2]I_2^j + [Nu_k(\vec{r}) + \varepsilon_3]I_1^k \\
&\quad + [Nu_k(\vec{r}') + \varepsilon_4]I_2^k \\
&= \frac{1}{2}\{[u_j(\vec{r}) - u_k(\vec{r})] - [u_j(\vec{r}') - u_k(\vec{r}')] + \varepsilon_5\}\int [\lambda_j|\delta(\psi_j^*\psi_j)| \\
&\quad + \lambda_k|\delta(\psi_k^*\psi_k)|]d\vec{r}_1\cdots d\vec{r}_N,
\end{aligned} \tag{19}$$

where $\varepsilon_i\to 0$, $i=1,2,3,4,5$, as $V\to\vec{r}$ and $V'\to\vec{r}'$. Because the expression in Eq. (19) is a higher-order infinitesimal, one concludes

$$u_j(\vec{r}) - u_k(\vec{r}) = u_j(\vec{r}') - u_k(\vec{r}'). \tag{20}$$

Hence $u_j(\vec{r})$ and $u_k(\vec{r})$ can differ only by a constant. Since $u_i(\vec{r}) = E_i/N - v_i(\vec{r})$, one can take $v_j(\vec{r}) = v_k(\vec{r})$ and incorporate the constant into E_j or E_k. It follows that every ψ_i is an eigenstate of the same external potential $v(\vec{r})$. If we further suppose that the excited states of $v(\vec{r})$ can only achieve stationarity and cannot achieve a minimum in the constrained search of $\langle\psi|\hat{T}+\hat{U}|\psi\rangle$, all ψ_i are ground states and all E_i are the same. This means that density $\rho(\vec{r})$ is ensemble v-representable.

The differentiability of $F[\rho]$ in Eqs. (1) and (14) at a v-representable density $\rho(\vec{r})$ was established by Englisch and Englisch [32] and by Lindgren and Salomonson [33]. Although their proofs were recently questioned by Lammert [34], the result was not precluded and is still deemed correct. The derivative is

$$\frac{\delta F[\rho]}{\delta\rho(\vec{r})} = C - v(\vec{r}), \tag{21}$$

where C is a constant.

Perdew *et al.* extended the domain of DFT functionals by considering the ensemble of mixed states for the electron system with a varying electron number [18,20]. In the ensemble extension, the universal functional is defined by

$$F[\rho] = \min_{\psi_{N-1},\psi_N\Rightarrow\rho}[(1-\omega)\langle\psi_{N-1}|\hat{T}+\hat{U}|\psi_{N-1}\rangle + \omega\langle\psi_N|\hat{T}+\hat{U}|\psi_N\rangle], \tag{22}$$

where wave functions ψ_{N-1} and ψ_N generate densities $\rho_{N-1}(\vec{r})$ and $\rho_N(\vec{r})$ of the $(N-1)$- and N-electron systems, respectively, $\rho(\vec{r}) = (1-\omega)\rho_{N-1}(\vec{r}) + \omega\rho_N(\vec{r})$, and $0\le\omega\le 1$. If the minimum in Eq. (22) is achieved by a pair of wave functions ψ_{N-1} and ψ_N that satisfy Eq. (2) and have continuous second derivatives, ψ_{N-1} and ψ_N are eigenstates of an external potential $v(\vec{r})$, since ψ_{N-1} minimizes $\langle\psi_{N-1}|\hat{T}+\hat{U}|\psi_{N-1}\rangle$ among wave functions generating $\rho_{N-1}(\vec{r})$ and ψ_N minimizes $\langle\psi_N|\hat{T}+\hat{U}|\psi_N\rangle$ among wave functions generating $\rho_N(\vec{r})$. Furthermore, if the excited states of this $v(\vec{r})$ can only achieve stationarity and cannot achieve a minimum in the constrained search, ψ_{N-1} and ψ_N are ground states and density $\rho(\vec{r})$ is ensemble v-representable. The proof is the same as that for Lieb's ensemble functional. It should be noted that ψ_{N-1} is a function of $\vec{r}_1,\ldots,\vec{r}_{N-1}$ and ψ_N is a function of $\vec{r}_1,\ldots,\vec{r}_N$. Thus ψ_{N-1} and ψ_N have different ground-state energies E_{N-1} and E_N. Differentiability of $F[\rho]$ in Eq. (22) at this $\rho(\vec{r})$ can be established as for Lieb's ensemble functional. The result is

$$\frac{\delta F[\rho]}{\delta\rho(\vec{r})} = (E_N - E_{N-1}) - v(\vec{r}). \tag{23}$$

The main difference between the functional in Eq. (22) and Lieb's ensemble functional is that for the latter, although λ_i varies, the electron number remains N, since $\int\delta\rho(\vec{r}_1)d\vec{r}_1 = N\sum_{i=1}^{\infty}\delta\lambda_i = 0$ according to Eq. (15). In Eq. (22), however, the variation of ω leads to the variation of the electron number by $\delta\omega$. Hence the electron number variation has been taken into consideration and Eq. (23) gives the completely determined derivative $\delta F/\delta\rho$ without arbitrary constant in it [20].

C. Time-dependent case

In TDDFT, the universal functional was originally defined by the action integral [23,24] and can be revised as [27]

$$B[\rho] = \operatorname{stat}_{\psi\Rightarrow\rho}\int_{t_0}^{t_1}\langle\psi|i\,\partial/\partial t - \hat{T} - \hat{U}|\psi\rangle dt. \tag{24}$$

The stationarity is searched for TD wave functions having the fixed initial state $\psi(\vec{r}_1,\ldots,\vec{r}_N,t_0)$ and generating density $\rho(\vec{r},t)$. However, a true TD wave function must satisfy the continuity equation

$$\frac{\partial(\psi^*\psi)}{\partial t} + \sum_{k=1}^{N}\nabla_k\cdot\vec{j}_k(\vec{r}_1,\ldots,\vec{r}_N,t) = 0, \tag{25}$$

where $\vec{j}_k$ is the TD current density kernel. Suppose the stationarity is achieved by a TD wave function ψ that satisfies Eq. (25) and has a continuous first derivative with respect to the time coordinate and continuous second derivatives with respect to the space coordinates. One can define

$$\phi(\vec{r}_1,\ldots,\vec{r}_N,t)=\frac{(i\,\partial/\partial t-\hat{T}-\hat{U})\psi(\vec{r}_1,\ldots,\vec{r}_N,t)}{\psi(\vec{r}_1,\ldots,\vec{r}_N,t)}. \quad (26)$$

Because Eq. (25) means $\partial(\psi^*\psi)/\partial t+i(\psi^*\hat{T}\psi-\psi\hat{T}\psi^*)=0$ and thus $(-i\,\partial\psi^*/\partial t-\hat{T}\psi^*)/\psi^*=(i\,\partial\psi/\partial t-\hat{T}\psi)/\psi$, ϕ is a real function. ϕ is also symmetric with respect to the space coordinates and continuous if $\psi\neq 0$. For the N-electron system, apart from the $2N$ fixed spatial points $\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N$, $\vec{r}'_1,\vec{r}'_2,\ldots,\vec{r}'_N$ and corresponding small regions $V_1,V_2,\ldots,V_N$, $V'_1,V'_2,\ldots,V'_N$ introduced in the static case, a fixed time t and a small time interval $[t,t+\Delta t]$ are also chosen. In the TD case, apart from the spatial restriction, $\delta\psi$ is chosen such that $\delta(\psi^*\psi)$ is nonzero only in $[t,t+\Delta t]$. We retain Eqs. (7)–(9) for every time in $[t,t+\Delta t]$ and define

$$I_1=\int_t^{t+\Delta t}dt\int_{V_1\times V_2\times\cdots\times V_N}\delta(\psi^*\psi)d\vec{r}_1\cdots d\vec{r}_N,$$

$$I_2=\int_t^{t+\Delta t}dt\int_{V_1\times V'_2\times\cdots\times V'_N}\delta(\psi^*\psi)d\vec{r}_1\cdots d\vec{r}_N,$$

$$I_3=\int_t^{t+\Delta t}dt\int_{V'_1\times V_2\times\cdots\times V_N}\delta(\psi^*\psi)d\vec{r}_1\cdots d\vec{r}_N,$$

and

$$I_4=\int_t^{t+\Delta t}dt\int_{V'_1\times V'_2\times\cdots\times V'_N}\delta(\psi^*\psi)d\vec{r}_1\cdots d\vec{r}_N.$$

Like Eq. (11), one obtains

$$\begin{aligned}\int_{t_0}^{t_1}dt\int\phi\delta(\psi^*\psi)d\vec{r}_1\cdots d\vec{r}_N=N!\{&[\phi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t)+\varepsilon_1]I_1\\&+[\phi(\vec{r}_1,\vec{r}'_2,\ldots,\vec{r}'_N,t)+\varepsilon_2]I_2\\&+[\phi(\vec{r}'_1,\vec{r}_2,\ldots,\vec{r}_N,t)+\varepsilon_3]I_3\\&+[\phi(\vec{r}'_1,\vec{r}'_2,\ldots,\vec{r}'_N,t)+\varepsilon_4]I_4\}\\=\frac{1}{4}\{&[\phi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t)\\&-\phi(\vec{r}_1,\vec{r}'_2,\ldots,\vec{r}'_N,t)]\\&-[\phi(\vec{r}'_1,\vec{r}_2,\ldots,\vec{r}_N,t)\\&-\phi(\vec{r}'_1,\vec{r}'_2,\ldots,\vec{r}'_N,t)]+\varepsilon_5\}\\&\times\int_{t_0}^{t_1}dt\int|\delta(\psi^*\psi)|d\vec{r}_1\cdots d\vec{r}_N,\end{aligned} \quad (27)$$

where $\varepsilon_i\to 0$, $i=1,2,3,4,5$, as $\Delta t\to 0$, $V_i\to\vec{r}_i$, $V'_i\to\vec{r}'_i$, $i=1,2,\ldots,N$. The fact that $\int_{t_0}^{t_1}dt\int\phi\delta(\psi^*\psi)d\vec{r}_1\cdots d\vec{r}_N$ is a higher-order infinitesimal leads to $\phi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N,t)-\phi(\vec{r}_1,\vec{r}'_2,\ldots,\vec{r}'_N,t)=\phi(\vec{r}'_1,\vec{r}_2,\ldots,\vec{r}_N,t)-\phi(\vec{r}'_1,\vec{r}'_2,\ldots,\vec{r}'_N,t)$. Hence $\phi(\vec{r}_1,\ldots,\vec{r}_N,t)=\sum_{i=1}^N v(\vec{r}_i,t)$ and Eq. (26) becomes

$$i\frac{\partial\psi}{\partial t}=(\hat{T}+\hat{U})\psi+\psi\sum_{i=1}^N v(\vec{r}_i,t). \quad (28)$$

This means that ψ satisfies the TD Schrödinger equation of some TD external potential $v(\vec{r},t)$ and density $\rho(\vec{r},t)$ is TD v-representable. The differentiability of $B[\rho]$ at the TD v-representable $\rho(\vec{r},t)$ can be established as in the static case. The result is

$$\frac{\delta B[\rho]}{\delta\rho(\vec{r},t)}=v(\vec{r},t). \quad (29)$$

D. Generalized case

DFT that treats all eigenstates of the N-electron system on the same footing depends on the generalization of Levy's minimum constrained search to a stationary constrained search [35], that is,

$$F[\rho,\mu]=\operatorname*{stat}_{\mu,\psi\Rightarrow\rho}\langle\psi|\hat{T}+\hat{U}|\psi\rangle, \quad (30)$$

where μ is an index used to distinguish different stationary points and corresponding values of $\langle\psi|\hat{T}+\hat{U}|\psi\rangle$ for the same density $\rho(\vec{r})$. The key point in our proof of Eq. (13) is that at the considered wave function, the first-order variation of $\langle\psi|\hat{T}+\hat{U}|\psi\rangle$ vanishes. In general, this condition is satisfied by wave functions that achieve stationarity but do not necessarily achieve a minimum in the constrained search. Hence our proof of Eq. (13) is also valid for the functional defined in Eq. (30). In fact, it is proven that if for a density the stationarity of Eq. (30) is achieved by a wave function that satisfies Eq. (2) and has continuous second derivatives, the stationary wave function is an eigenstate of some external potential. This provides a sufficient condition for Lemma II of Ref. [35]. The lemma was proven in that paper on the premise that $F[\rho,\mu]$ is differentiable.

III. CONCLUSION

It is examined whether the stationary wave function obtained in DFT constrained search satisfies the Schrödinger equation of some external potential. Sufficient conditions are suggested and the proof is presented. In both usual DFT and TDDFT, if the stationary wave function satisfies the continuity equation for the current density kernel, and all its derivatives that will appear in the Schrödinger equation are continuous, there will always exist an external potential that yields the Schrödinger equation for the stationary wave function. In the usual DFT, the continuity equation reduces to the steadiness condition and the stationary wave function is an eigenstate of the external potential. Of special importance is the case for the minimizing wave function obtained in the constrained search. These conclusions also provide indirect conditions for v-representability in both usual DFT and TDDFT.

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